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(54) LITHIUM ION-TRANSMISSIBLE GLASS CERAMICS AND BATTERY AND GAS SENSOR USING IT

(57)Abstract:
PROBLEM TO BE SOLVED: To provide lithium ion-transmissible glass ceramic requiring only simple manufacture and thermally strong and chemically stabilized, by depositing Li1+x+YMxTi2-xSiYP3-YO12 by heat treatment after fused formation, by including P2O5; 26 to 40%, SiO2; 0.5 to 12% TiO2; 30 to 45%, M2O3 (while M=Al, Ga); 5 to 10%, Li2O; 10 to 18% in mol%.
SOLUTION: In the above formula, relationship 0≤X≤0.4, 0<Y≤0.6 are designated. For the purpose of ion-transmissible glass ceramics, the above material is measured by a specific ratio in its weight and after mixing it uniformly, it is placed in a platinum crucible, heated and fused by an electric furnace. Firstly, the materials is resolved at 700° C so as to evaporate gas component, then the temperature is raised up to 1400 to 1500° C and the material is fused at this temperature for 1 to 2 hours. With regard to thus obtained glass, by making heat treatment for 12 hours at 680 to 800° C, subsequently making heat treatment for 24 hours at a temperature higher than the above one, Li1+x+YMxTi2-xSiYP3-YO12 is deposited as a principal crystal phase, so as to obtian high ion-transmissible glass ceramics.

CLAIMS

[Claim(s)]
[Claim 1]By mol% display, 26 to 40% of P_2O_5, 0.5 to 12% of SiO_2, 30 to 45% of TiO_2, and M_2O_3 (however, M=aluminum, Ga) Contain 5 to 10%, and Li_2O 10 -18%, and by heat treatment after melt molding. Lithium-ion-conductivity crystallized glass depositing $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$ (however, 0<=X<=0.4, 0< Y<=0.6).
[Claim 2]By mol% display, 26 to 40% of P_2O_5, 0.5 to 12% of SiO_2, Contain 32 to 45% of TiO_2, 5 to 10% of aluminum_2O_3, and Li_2O 10 -18%, and by heat treatment after melt molding. The crystallized glass according to claim 1 depositing $Li_{1+X+Y}\text{aluminum}_XTi_{2-X}Si_YP_{3-Y}O_{12}$ (however, 0<=X<=0.4, 0< Y<=0.6).
[Claim 3]By mol% display, 26 to 40% of P_2O_5, 0.5 to 12% of SiO_2, Contain 32 to 45% of TiO_2, 5 to 10% of Ga_2O_3, and Li_2O 10 -18%, and by heat treatment after melt molding. The crystallized glass according to claim 1 depositing $Li_{1+X+Y}Ga_XTi_{2-X}Si_YP_{3-Y}O_{12}$ (however, 0<=X<=0.4, 0< Y<=0.6).
[Claim 4]A solid electrolyte for cells which consists of the crystallized glass according to any one of claims 1 to 3.
[Claim 5]A solid electrolyte for gas sensors which consists of the crystallized glass according to any one of claims 1 to 3.
[Claim 6]A lithium ion battery using the lithium-ion-conductivity crystallized glass according to any one of claims 1 to 3.
[Claim 7]A gas sensor using the lithium-ion-conductivity crystallized glass according to any one of claims 1 to 3.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]Ionic conductivity of this invention is high, and is thermally and chemically stable, and manufacture is related with easy lithium-ion-conductivity crystallized glass.
[0002]
[Description of the Prior Art]As for progress of electronics in recent years, development of a long lasting cell is strongly desired especially with high energy density as a power supply of those apparatus with the miniaturization of electronic equipment, a weight saving, and highly-efficient-izing. Since the oxidation-reduction potential of lithium elements of Li/Li^+ is the highest in all metal and the mass per mol is dramatically small, the lithium cell can obtain high energy density from other cells. When using a lithium ion conductive solid electrolyte, since it is possible to make it thin,-izing of the cell can be carried out [thin film], and the energy density per volume can be improved greatly.
[0003]In addition to the miniaturization of a cell and thin-film-izing being difficult for the lithium ion battery put in practical use now, since an electrolyte is organic electrolysis liquid, we are anxious about liquid leakage or the danger of ignition. If it is transposed to an inorganic electrolyte, it will be thought that a reliable totally-solid battery can be constituted.
[0004]The choke damp emitted by combustion of a fossil fuel is the main factor of the greenhouse effect which poses a problem in recent years.
For this reason, the continuous surveillance of choke-damp concentration is needed.
Therefore, establishment of these detection systems is gaining in the importance, in order to maintain the comfortable living environment of future human society.
[0005]Although the choke-damp detection system with which practical use is presented has a common type using infrared absorption now, a device is large-sized, and is expensive and it has in contamination the fault that it is weak. Therefore, these days, research of the compact carbon dioxide gas sensor which used the solid electrolyte is done briskly. In it, many researches using a lithium ion solid electrolyte are reported.
[0006]However, in order to realize these, conductivity is high, it is chemically stable, and development of a solid electrolyte strong against heat is indispensable.
[0007]As what conductivity is the highest in a solid electrolyte by the present, and exceeds 10^{-3}S/cm at a room temperature, A Li_3N single crystal [Applied Physics letters, 30 (1977) 621-622.], $LiI-Li_2S-P_2S_5$ [Solid State Ionics, 5(1981)663.], $LiI-Li_2S-B_2S_3$[Mat.Res.Bull. and 18 (1983) 189.] and $LiI-Li_2S-SiS_4$[J. The glass of Solid State Chem. and a 69 (1987) 252.] system is known.
[0008]However, such materials are difficult to produce, chemical stability is not good, either, and heat has the fault that it is weak. Since decomposition voltage is low especially when using it as an electrolyte of a solid state battery, it has the fatal fault that high terminal voltage cannot be taken.
[0009]On the other hand, the possibility of utilization is high if a room temperature shows high conductivity, since an oxide stock lithium solid electrolyte does not have the above faults, and decomposition voltage is also higher than 3V. In oxide glass, increasing conductivity is known by increasing the concentration of a lithium ion. However, since it vitrifies, even if it uses rapid quenching, there is a limit in the increase in the concentration of a lithium ion, and what has the high conductivity in a room temperature has not reached 10^{-6}S/cm.
[0010]Although JP,8-2239218,A has the statement of the gas sensor which used the lithium-ion-conductivity

glass thin film, That in which the conductivity of the lithium-ion-conductivity glass thin film by this has 6.1×10^{-7}S/cm from 1.7×10^{-7} and not a by no means high thing but higher conductivity is needed.
[0011]The conductivity of Li_{1+X}aluminum$_XTi_{2-X}(PO_4)_3$ is the highest in oxide ceramics (sintered compact), [J. in which the value is 7×10^{-4}S/cm at a room temperature (at the time of X= 0.3) Electrochem.Soc. and 137 (1990) 1023.]. Although oxide ceramics are advantageous in respect of conductivity compared with oxide glass, it has the fault that a manufacturing process is complicated, a moldability is bad, and thin-film-izing is difficult.
[0012]
[Problem(s) to be Solved by the Invention]As stated above, the conventional lithium ion solid electrolyte had low conductivity, and it had the technical problem that a miniaturization and thin-film-izing were difficult. This invention solves these technical problems, provides crystallized glass with the very high lithium ion conductivity of reaching 1.5×10^{-3}S/cm at a room temperature, and is realizing a highly efficient lithium cell and gas sensor using this crystallized glass further.
[0013]
[Means for Solving the Problem]It was said in a top that Li_{1+X}aluminum$_XTi_{2-X}(PO_4)_3$ ceramics show conductivity of a 10^{-4}S/cm stand at a room temperature. However, a stoma and a grain boundary which can never be lost exist in these ceramics. These existence serves to reduce conductivity. Since a stoma can be lost and a grain boundary may also be improved if crystallized glass including the above conductive crystals is obtained, it is expectable that a solid electrolyte with higher conductivity is obtained. Since it can also be made various shape and a thin film taking advantage of the characteristic of glass in the case of crystallized glass, a merit is larger than ceramics produced with a sintering process practically.
[0014]As a result of repeating research based on such a view, this invention person P_2O_5, SiO_2, TiO_2, and M_2O_3. Glass containing a (M=aluminum, Ga) Li_2O ingredient is produced, [however,] By depositing conductive crystal $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$ from glass using heat treatment method. It succeeds in obtaining crystallized glass with very high lithium ion conductivity of reaching 1.5×10^{-3}S/cm at a room temperature, and came to make this invention.
[0015]Namely, the invention according to claim 1 is a mol% display in the above-mentioned lithium-ion-conductivity crystallized glass, 26 to 40% of P_2O_5, 0.5 to 12% of SiO_2, Contain 30 to 45% of TiO_2, 5 to 10% of M_2O_3 (however, M=aluminum, Ga), and Li_2O 10 -18%, and by heat treatment after melt molding. It is characterized by $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$ (however, $0 <= X <= 0.4$, $0 < Y <= 0.6$) depositing.
[0016]The invention according to claim 2 is a mol% display in the above-mentioned lithium-ion-conductivity crystallized glass, 26 to 40% of P_2O_5, 0.5 to 12% of SiO_2, Contain 32 to 45% of TiO_2, 5 to 10% of aluminum$_2O_3$, and Li_2O 10 -18%, and by heat treatment after melt molding. It is characterized by Li_{1+X+Y}aluminum$_XTi_{2-X}Si_YP_{3-Y}O_{12}$ (however, $0 <= X <= 0.4$, $0 < Y <= 0.6$) depositing.
[0017]The invention according to claim 3 is a mol% display in the above-mentioned lithium-ion-conductivity crystallized glass, 26 to 40% of P_2O_5, 0.5 to 12% of SiO_2, Contain 32 to 45% of TiO_2, 5 to 10% of Ga_2O_3, and Li_2O 10 -18%, and by heat treatment after melt molding. It is characterized by $Li_{1+X+Y}Ga_XTi_{2-X}Si_YP_{3-Y}O_{12}$ (however, $0 <= X <= 0.4$, $0 < Y <= 0.6$) depositing.
[0018]The invention according to claim 4 is characterized by a solid electrolyte for cells consisting of said crystallized glass according to any one of claims 1 to 3.
[0019]The invention according to claim 5 is characterized by a solid electrolyte for gas sensors consisting of said crystallized glass according to any one of claims 1 to 3.
[0020]A presentation of crystallized glass of this invention can be displayed by an oxide basis like original glass. A reason which limited a presentation of crystallized glass as mentioned above, After melting cooling, by heat treatment $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$. ($0 <= X <= 0.4$, $0 <= Y <= 0.6$) can obtain precise crystallized glass which deposited as a main crystal, and the crystallized glass is in very high lithium ion conductivity being shown at a room temperature. [however,] Although $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$ deposits also in composition ranges other than the above, since the rate is low, its conductivity is small.
[0021]Especially an effect of SiO_2 is important in the above-mentioned ingredient. A vitrification range not only

becomes large, but improved by adding SiO_2. [the melting nature of glass and thermal stability's] Conductivity which exceeds 10^{-3}S/cm in a wide composition range was shown after heat treatment.
[0022]It is divalent metals, such as trivalent metals, such as B, In, Sc, Fe, and Cr, and Mg, and Zn, in a part of aluminum or Ga ingredient, and it is Zr in a part of Ti, and it is also possible to replace a part of Si in germanium. However, those quantity should be made less than 5mol%, and if it adds more, conductivity will fall substantially.
[0023]In order to improve the melting nature of glass, it is also possible to add As_2O_3, Sb_2O_3, Ta_2O_5, CdO, PbO, etc., but. Those quantity should be restricted to less than 3mol%, and if it adds more, conductivity will become small gradually with increase of an addition.
[0024]
[Embodiment of the Invention]The lithium-ion-conductivity crystallized glass of this invention is producible by the following method. That is, after carrying out weighing of the starting material by a predetermined ratio and mixing uniformly, it puts into a platinum crucible and heat melting is carried out with an electric furnace. First, a raw material is disassembled at 700 **, gas constituents are evaporated, then, temperature is raised to 1400-1500 **, and it fuses at the temperature for 1 to 2 hours. Then, the cast of the solution is carried out on a griddle, and tabular glass is produced. In this way, by heat-treating at 680-800 ** about the obtained glass for 24 hours for 12 hours at a temperature succeedingly higher further 200-350 ** than it, The high lithium-ion-conductivity crystallized glass in which $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$ deposits as a main crystal is obtained.
[0025]The same result is obtained even if it uses one-step heat treatment, without using the above two-step heat treatments about a heat treatment condition. However, in order not to make a sample generate a crack in this case, temperature up must be carried out at speed quite late to heat treatment temperature. In this case, since a long time is required dramatically, it is not efficient. Therefore, above-mentioned two-step heat treatment method is desirable. The crystallized glass of this invention can also be produced by cooling slowly from the state where melting was carried out, without passing through a vitreous state. However, in order to obtain the precise sample which does not have a crack in this case, a cooling rate must be adjusted for every presentation and must be controlled precisely.
[0026]
[Example]Hereafter, although a concrete example explains this invention, this invention is not limited to these examples.
[0027][Example 1] As a raw material, use $NH_4H_2PO_4$, SiO_2, TiO_2, aluminum$(OH)_3$, and Li_2CO_3, and these by mol%. After having carried out weighing so that it might become the presentation $32P_2O_5$-$8SiO_2$-$41TiO_2$-5aluminum$_2O_3$-$14Li_2O$, and mixing uniformly, it put into the platinum crucible and heat melting was carried out with the electric furnace. First, the raw material was disassembled at 700 **, CO_2, NH_3, and an H_2O ingredient were evaporated, then, temperature up was carried out to 1450 **, and it fused at the temperature for 1.5 hours. Then, the cast was carried out on the griddle which warmed glass melt beforehand, and uniform tabular glass was produced. In order to remove distortion of glass, it annealed at 550 ** for 2 hours. In this way, after cutting the obtained glass in size of 20 mm x 20 mm and grinding both sides, precise crystallized glass was obtained by subsequently performing heat treatment of 24 hours at 1000 ** at 800 ** for 12 hours. As for the crystal phase which deposited, it was checked by powder X-ray diffractometry that it is Li_{1+X+Y}aluminum$_XTi_{2-X}Si_YP_{3-Y}O_{12}$. The crystallized glass showed very high conductivity called 1.5×10^{-3}S/cm at the room temperature.
[0028][Examples 2-6] The sample to Examples 2-6 was produced by the same method as Example 1. The conductivity in each room temperature was summarized in Table 1. The conductivity of the crystallized glass by all the examples was measured in the range of 10^{-2} - $3\times10^{+7}$Hz by alternating current impedance. It asked for resistance (sum of particles and grain boundary resistance) of the sample from the call call plot, and conductivity was calculated according to equation sigma= (t/A) (1/R). (However, sigma:conductivity, the thickness of t:sample, area of A:electrode, R: Resistance of a sample)
[0029]
[Table 1]

単位；ｗｔ％

実施例			
Ｎｏ	１	２	３
P_2O_5	３２	３３．５	３０
SiO_2	８	６	１０
TiO_2	４１	４２	４０
Al_2O_3	５	５	５
Ga_2O_3			
Li_2O	１４	１３．５	１５
室温での伝導率（Ｓ／ｃｍ）	1.5×10^{-3}	1.0×10^{-3}	1.2×10^{-3}

単位；ｗｔ％

実施例			
Ｎｏ	４	５	６
P_2O_5	３５	３２	３５
SiO_2	４	８	４
TiO_2	３８	４１	３８
Al_2O_3	８		５
Ga_2O_3		５	３
Li_2O	１５	１４	１５
室温での伝導率（Ｓ／ｃｍ）	1.1×10^{-3}	1.2×10^{-3}	1.0×10^{-3}

[0030][Example 8] As a typical example of a lithium cell, an example (sectional view) of a flat type cell is shown in drawing 2. This cell The negative electrode can 6, the negative pole collector 4 (a conductive thin film, thin films, etc., such as aluminum and stainless steel, are used.), It comprises the negative electrode 2, the Li-ion conductivity crystallized glass 1, the anode 3, the positive pole collector 5 (a conductive thin film, thin films, etc., such as aluminum and stainless steel, are used.), the positive electrode can 7, and the insulating packing 8 (polypropylene etc.). Positive/negative each poles 2 and 3 are dedicated in the case which counters via Li-ion conductivity crystallized glass, and the positive-and-negative-poles cans 6 and 7 form. As for the anode 3, the negative electrode 2 is connected to the negative electrode can 6 via the negative pole collector 4 at the positive electrode can 7 via the positive pole collector 5. The chemical energy produced inside the cell can be taken out now from both the terminals of a positive electrode can and the negative electrode cans 6 and 7 to the exterior as electrical energy.
[0031]About the member which constitutes the cell by this invention, it is possible except a solid electrolyte portion to use various materials currently conventionally used besides the substance indicated above.
[0032]The thickness of Li-ion conductivity crystallized glass shall be thin, and shall be 0.5 mm or less preferably at least 1 mm or less here. Various kinds of devices and announcements are made and the material of the anode 3 has $LiCoO_2$, $Li_{1+X}V_3O_8$, etc. as a typical example. Various kinds of devices and announcements are similarly made about the material of the negative electrode 2, and there are $Li_4Ti_5O_{12}$, carbon, etc. as a typical example.
[0033]About positive/negative each poles 2 and 3 formed in both sides to which Li-ion conductivity crystallized glass counters, and the collectors 4 and 5 formed in positive/negative each pole. The method of making these which were created beforehand piling up mutually one by one, and attaching them, The method of forming a pole

and a charge collector one by one with an ion spattering method, a CVD method, screen printing, the applying method, a sol gel process, the ion plating method, an ion-beam-deposition method, an MBE technique, a vacuum deposition method, electron beam evaporation method, etc. can also be used.
[0034]A comparative example to a solid electrolyte Titanium oxide:1.7 mol, lithium carbonate:0.7 mol, Ammonium phosphate : 3.0 mol and aluminum oxide:0.2 mol are mixed in an agate mortar, After carrying out pressing and making it a pellet type, the agate mortar ground again the fired material obtained by calcinating for 2 hours at 900 **, pressing of what passed the screen of 400 meshes was again carried out to the pellet type, it sintered at 1000 ** for 2 hours, and what was processed laminated was used as a solid electrolyte.
[0035][Example 9] As a typical example of a gas sensor, an example (sectional view) of a carbonic acid gas sensor is shown in drawing 3. Up-and-down both sides of the Li-ion conductivity crystallized glass by the above-mentioned example to 1-2 mm in thickness, The mixture of a metallic carbonate layer, and desirable lithium carbonate or lithium carbonate and other carbonate is preferably formed in one side of the polished surface with an ion spattering method after grinding to 0.5 mm or less still more preferably 1 mm or less. Subsequently, stick on this field the platinum mesh which connected the lead, a carbonate layer is made to form again, and a platinum mesh is fixed. The platinum thin film formed with vacuum deposition is formed in another field, and a lead is connected to this. Since the electromotive force according to carbon dioxide gas concentration arises in inter-electrode according to the dissociation equilibrium of carbonate by the carbon dioxide in a carbon dioxide gaseous mixture, this sensor can know carbon dioxide gas concentration by measuring this electromotive force.
[0036]The method of forming a carbonate layer and an electrode layer can be formed with a CVD method, screen printing, the applying method, a sol gel process, the ion plating method, an ion-beam-deposition method, an MBE technique, a vacuum deposition method, electron beam evaporation method, etc. besides the above.
[0037]
[Effect of the Invention]As explained above, the lithium-ion-conductivity crystallized glass by this invention has very high lithium ion conductivity, and. Simply and chemically, since [stable] it is thermally strong, production begins a cell (a fuel cell is also included) and a gas sensor, and the application of it to various electrochemical devices is attained.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention]Ionic conductivity of this invention is high, and is thermally and chemically stable, and manufacture is related with easy lithium-ion-conductivity crystallized glass.

[Translation done.]

PRIOR ART

[Description of the Prior Art]As for progress of electronics in recent years, development of a long lasting cell is strongly desired especially with high energy density as a power supply of those apparatus with the miniaturization of electronic equipment, a weight saving, and highly-efficient-izing. Since the oxidation-reduction potential of lithium elements of Li/Li^+ is the highest in all metal and the mass per mol is dramatically small, the lithium cell can obtain high energy density from other cells. When using a lithium ion conductive solid electrolyte, since it is possible to make it thin,-izing of the cell can be carried out [thin film], and the energy density per volume can be improved greatly.
[0003]In addition to the miniaturization of a cell and thin-film-izing being difficult for the lithium ion battery put in practical use now, since an electrolyte is organic electrolysis liquid, we are anxious about liquid leakage or the danger of ignition. If it is transposed to an inorganic electrolyte, it will be thought that a reliable totally-solid battery can be constituted.
[0004]The choke damp emitted by combustion of a fossil fuel is the main factor of the greenhouse effect which poses a problem in recent years.
For this reason, the continuous surveillance of choke-damp concentration is needed.
Therefore, establishment of these detection systems is gaining in the importance, in order to maintain the comfortable living environment of future human society.
[0005]Although the choke-damp detection system with which practical use is presented has a common type using infrared absorption now, a device is large-sized, and is expensive and it has in contamination the fault that it is weak. Therefore, these days, research of the compact carbon dioxide gas sensor which used the solid electrolyte is done briskly. In it, many researches using a lithium ion solid electrolyte are reported.
[0006]However, in order to realize these, conductivity is high, it is chemically stable, and development of a solid electrolyte strong against heat is indispensable.
[0007]As what conductivity is the highest in a solid electrolyte by the present, and exceeds 10^{-3}S/cm at a room temperature, A Li_3N single crystal [Applied Physics letters, 30 (1977) 621-622.], $LiI-Li_2S-P_2S_5$ [Solid State Ionics, 5(1981)663.], $LiI-Li_2S-B_2S_3$[Mat.Res.Bull. and 18 (1983) 189.] and $LiI-Li_2S-SiS_4$[J. The glass of Solid State Chem. and a 69 (1987) 252.] system is known.
[0008]However, such materials are difficult to produce, chemical stability is not good, either, and heat has the fault that it is weak. Since decomposition voltage is low especially when using it as an electrolyte of a solid state battery, it has the fatal fault that high terminal voltage cannot be taken.
[0009]On the other hand, the possibility of utilization is high if a room temperature shows high conductivity, since an oxide stock lithium solid electrolyte does not have the above faults, and decomposition voltage is also higher than 3V. In oxide glass, increasing conductivity is known by increasing the concentration of a lithium ion. However, since it vitrifies, even if it uses rapid quenching, there is a limit in the increase in the concentration of a lithium ion, and what has the high conductivity in a room temperature has not reached 10^{-6}S/cm.
[0010]Although JP,8-2239218,A has the statement of the gas sensor which used the lithium-ion-conductivity glass thin film, That in which the conductivity of the lithium-ion-conductivity glass thin film by this has 6.1×10^{-7}S/cm from 1.7×10^{-7} and not a by no means high thing but higher conductivity is needed.
[0011]The conductivity of Li_{1+X}aluminum$_X Ti_{2-X}(PO_4)_3$ is the highest in oxide ceramics (sintered compact), [J. in which the value is 7×10^{-4}S/cm at a room temperature (at the time of X= 0.3) Electrochem.Soc. and 137 (1990) 1023.]. Although oxide ceramics are advantageous in respect of conductivity compared with oxide glass, it has the

fault that a manufacturing process is complicated, a moldability is bad, and thin-film-izing is difficult.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention]As explained above, the lithium-ion-conductivity crystallized glass by this invention has very high lithium ion conductivity, and. Simply and chemically, since [stable] it is thermally strong, production begins a cell (a fuel cell is also included) and a gas sensor, and the application of it to various electrochemical devices is attained.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]As stated above, the conventional lithium ion solid electrolyte had low conductivity, and it had the technical problem that a miniaturization and thin-film-izing were difficult. This invention solves these technical problems, provides crystallized glass with the very high lithium ion conductivity of reaching $1.5x10^{-3}$S/cm at a room temperature, and is realizing a highly efficient lithium cell and gas sensor using this crystallized glass further.

[Translation done.]

MEANS

[Means for Solving the Problem]It was said in a top that Li_{1+X}aluminum$_XTi_{2-X}(PO_4)_3$ ceramics show conductivity of a 10 $^{-4}$S/cm stand at a room temperature. However, a stoma and a grain boundary which can never be lost exist in these ceramics. These existence serves to reduce conductivity. Since a stoma can be lost and a grain boundary may also be improved if crystallized glass including the above conductive crystals is obtained, it is expectable that a solid electrolyte with higher conductivity is obtained. Since it can also be made various shape and a thin film taking advantage of the characteristic of glass in the case of crystallized glass, a merit is larger than ceramics produced with a sintering process practically.

[0014]As a result of repeating research based on such a view, this invention person P_2O_5, SiO_2, TiO_2, and M_2O_3. Glass containing a (M=aluminum, Ga) Li_2O ingredient is produced, [however,] By depositing conductive crystal $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$ from glass using heat treatment method. It succeeds in obtaining crystallized glass with very high lithium ion conductivity of reaching 1.5x10 $^{-3}$S/cm at a room temperature, and came to make this invention.

[0015]Namely, the invention according to claim 1 is a mol% display in the above-mentioned lithium-ion-conductivity crystallized glass, 26 to 40% of P_2O_5, 0.5 to 12% of SiO_2, Contain 30 to 45% of TiO_2, 5 to 10% of M_2O_3 (however, M=aluminum, Ga), and Li_2O 10 -18%, and by heat treatment after melt molding. It is characterized by $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$ (however, 0<=X<=0.4, 0< Y<=0.6) depositing.

[0016]The invention according to claim 2 is a mol% display in the above-mentioned lithium-ion-conductivity crystallized glass, 26 to 40% of P_2O_5, 0.5 to 12% of SiO_2, Contain 32 to 45% of TiO_2, 5 to 10% of aluminum$_2O_3$, and Li_2O 10 -18%, and by heat treatment after melt molding. It is characterized by Li_{1+X+Y}aluminum$_XTi_{2-X}Si_YP_{3-Y}O_{12}$ (however, 0<=X<=0.4, 0< Y<=0.6) depositing.

[0017]The invention according to claim 3 is a mol% display in the above-mentioned lithium-ion-conductivity crystallized glass, 26 to 40% of P_2O_5, 0.5 to 12% of SiO_2, Contain 32 to 45% of TiO_2, 5 to 10% of Ga_2O_3, and Li_2O 10 -18%, and by heat treatment after melt molding. It is characterized by $Li_{1+X+Y}Ga_XTi_{2-X}Si_YP_{3-Y}O_{12}$ (however, 0<=X<=0.4, 0< Y<=0.6) depositing.

[0018]The invention according to claim 4 is characterized by a solid electrolyte for cells consisting of said crystallized glass according to any one of claims 1 to 3.

[0019]The invention according to claim 5 is characterized by a solid electrolyte for gas sensors consisting of said crystallized glass according to any one of claims 1 to 3.

[0020]A presentation of crystallized glass of this invention can be displayed by an oxide basis like original glass. A reason which limited a presentation of crystallized glass as mentioned above, After melting cooling, by heat treatment $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$. (0<=X<=0.4, 0<=Y<=0.6) can obtain precise crystallized glass which deposited as a main crystal, and the crystallized glass is in very high lithium ion conductivity being shown at a room temperature. [however,] Although $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$ deposits also in composition ranges other than the above, since the rate is low, its conductivity is small.

[0021]Especially an effect of SiO_2 is important in the above-mentioned ingredient. A vitrification range not only becomes large, but improved by adding SiO_2. [the melting nature of glass and thermal stability's] Conductivity which exceeds 10 $^{-3}$S/cm in a wide composition range was shown after heat treatment.

[0022]It is divalent metals, such as trivalent metals, such as B, In, Sc, Fe, and Cr, and Mg, and Zn, in a part of aluminum or Ga ingredient, and it is Zr in a part of Ti, and it is also possible to replace a part of Si in germanium. However, those quantity should be made less than 5mol%, and if it adds more, conductivity will fall substantially.
[0023]In order to improve the melting nature of glass, it is also possible to add As_2O_3, Sb_2O_3, Ta_2O_5, CdO, PbO, etc., but. Those quantity should be restricted to less than 3mol%, and if it adds more, conductivity will become small gradually with increase of an addition.
[0024]
[Embodiment of the Invention]The lithium-ion-conductivity crystallized glass of this invention is producible by the following method. That is, after carrying out weighing of the starting material by a predetermined ratio and mixing uniformly, it puts into a platinum crucible and heat melting is carried out with an electric furnace. First, a raw material is disassembled at 700 **, gas constituents are evaporated, then, temperature is raised to 1400-1500 **, and it fuses at the temperature for 1 to 2 hours. Then, the cast of the solution is carried out on a griddle, and tabular glass is produced. In this way, by heat-treating at 680-800 ** about the obtained glass for 24 hours for 12 hours at a temperature succeedingly higher further 200-350 ** than it, The high lithium-ion-conductivity crystallized glass in which $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$ deposits as a main crystal is obtained.
[0025]The same result is obtained even if it uses one-step heat treatment, without using the above two-step heat treatments about a heat treatment condition. However, in order not to make a sample generate a crack in this case, temperature up must be carried out at speed quite late to heat treatment temperature. In this case, since a long time is required dramatically, it is not efficient. Therefore, above-mentioned two-step heat treatment method is desirable. The crystallized glass of this invention can also be produced by cooling slowly from the state where melting was carried out, without passing through a vitreous state. However, in order to obtain the precise sample which does not have a crack in this case, a cooling rate must be adjusted for every presentation and must be controlled precisely.

[Translation done.]

EXAMPLE

[Example]Hereafter, although a concrete example explains this invention, this invention is not limited to these examples.
[0027][Example 1] As a raw material, use $NH_4H_2PO_4$, SiO_2, TiO_2, aluminum(OH) $_3$, and Li_2CO_3, and these by mol%. After having carried out weighing so that it might become the presentation 32P $_2O_5$-8SiO_2-41TiO_2-5aluminum$_2O_3$-14Li_2O, and mixing uniformly, it put into the platinum crucible and heat melting was carried out with the electric furnace. First, the raw material was disassembled at 700 **, CO_2, NH_3, and an H_2O ingredient were evaporated, then, temperature up was carried out to 1450 **, and it fused at the temperature for 1.5 hours. Then, the cast was carried out on the griddle which warmed glass melt beforehand, and uniform tabular glass was produced. In order to remove distortion of glass, it annealed at 550 ** for 2 hours. In this way, after cutting the obtained glass in size of 20 mm x 20 mm and grinding both sides, precise crystallized glass was obtained by subsequently performing heat treatment of 24 hours at 1000 ** at 800 ** for 12 hours. As for the crystal phase which deposited, it was checked by powder X-ray diffractometry that it is Li_{1+X+Y}aluminum$_X Ti_{2-X}Si_Y P_{3-Y}O_{12}$. The crystallized glass showed very high conductivity called 1.5x10 $^{-3}$S/cm at the room temperature.
[0028][Examples 2-6] The sample to Examples 2-6 was produced by the same method as Example 1. The conductivity in each room temperature was summarized in Table 1. The conductivity of the crystallized glass by all the examples was measured in the range of 10 $^{-2}$ - 3x10^{+7}Hz by alternating current impedance. It asked for resistance (sum of particles and grain boundary resistance) of the sample from the call call plot, and conductivity was calculated according to equation sigma= (t/A) (1/R). (However, sigma:conductivity, the thickness of t:sample, area of A:electrode, R: Resistance of a sample)
[0029]
[Table 1]

単位；wt%

実施例			
No	1	2	3
P_2O_5	32	33.5	30
SiO_2	8	6	10
TiO_2	41	42	40
Al_2O_3	5	5	5
Ga_2O_3			
Li_2O	14	13.5	15
室温での伝導率 (S/cm)	1.5×10^{-3}	1.0×10^{-3}	1.2×10^{-3}

単位；wt%

実施例			
No	4	5	6
P_2O_5	35	32	35
SiO_2	4	8	4
TiO_2	38	41	38
Al_2O_3	8		5
Ga_2O_3		5	3
Li_2O	15	14	15
室温での伝導率 (S/cm)	1.1×10^{-3}	1.2×10^{-3}	1.0×10^{-3}

[0030][Example 8] As a typical example of a lithium cell, an example (sectional view) of a flat type cell is shown in drawing 2. This cell The negative electrode can 6, the negative pole collector 4 (a conductive thin film, thin films, etc., such as aluminum and stainless steel, are used.), It comprises the negative electrode 2, the Li-ion conductivity crystallized glass 1, the anode 3, the positive pole collector 5 (a conductive thin film, thin films, etc., such as aluminum and stainless steel, are used.), the positive electrode can 7, and the insulating packing 8 (polypropylene etc.). Positive/negative each poles 2 and 3 are dedicated in the case which counters via Li-ion conductivity crystallized glass, and the positive-and-negative-poles cans 6 and 7 form. As for the anode 3, the negative electrode 2 is connected to the negative electrode can 6 via the negative pole collector 4 at the positive electrode can 7 via the positive pole collector 5. The chemical energy produced inside the cell can be taken out now from both the terminals of a positive electrode can and the negative electrode cans 6 and 7 to the exterior as electrical energy.

[0031]About the member which constitutes the cell by this invention, it is possible except a solid electrolyte portion to use various materials currently conventionally used besides the substance indicated above.

[0032]The thickness of Li-ion conductivity crystallized glass shall be thin, and shall be 0.5 mm or less preferably at least 1 mm or less here. Various kinds of devices and announcements are made and the material of the anode 3 has $LiCoO_2$, $Li_{1+X}V_3O_8$, etc. as a typical example. Various kinds of devices and announcements are similarly made about the material of the negative electrode 2, and there are $Li_4Ti_5O_{12}$, carbon, etc. as a typical example.

[0033]About positive/negative each poles 2 and 3 formed in both sides to which Li-ion conductivity crystallized glass counters, and the collectors 4 and 5 formed in positive/negative each pole. The method of making these which were created beforehand piling up mutually one by one, and attaching them, The method of forming a pole

and a charge collector one by one with an ion spattering method, a CVD method, screen printing, the applying method, a sol gel process, the ion plating method, an ion-beam-deposition method, an MBE technique, a vacuum deposition method, electron beam evaporation method, etc. can also be used.

[0034]A comparative example to a solid electrolyte Titanium oxide:1.7 mol, lithium carbonate:0.7 mol, Ammonium phosphate : 3.0 mol and aluminum oxide:0.2 mol are mixed in an agate mortar, After carrying out pressing and making it a pellet type, the agate mortar ground again the fired material obtained by calcinating for 2 hours at 900 **, pressing of what passed the screen of 400 meshes was again carried out to the pellet type, it sintered at 1000 ** for 2 hours, and what was processed laminated was used as a solid electrolyte.

[0035][Example 9] As a typical example of a gas sensor, an example (sectional view) of a carbonic acid gas sensor is shown in drawing 3. Up-and-down both sides of the Li-ion conductivity crystallized glass by the above-mentioned example to 1-2 mm in thickness, The mixture of a metallic carbonate layer, and desirable lithium carbonate or lithium carbonate and other carbonate is preferably formed in one side of the polished surface with an ion spattering method after grinding to 0.5 mm or less still more preferably 1 mm or less. Subsequently, stick on this field the platinum mesh which connected the lead, a carbonate layer is made to form again, and a platinum mesh is fixed. The platinum thin film formed with vacuum deposition is formed in another field, and a lead is connected to this. Since the electromotive force according to carbon dioxide gas concentration arises in inter-electrode according to the dissociation equilibrium of carbonate by the carbon dioxide in a carbon dioxide gaseous mixture, this sensor can know carbon dioxide gas concentration by measuring this electromotive force.

[0036]The method of forming a carbonate layer and an electrode layer can be formed with a CVD method, screen printing, the applying method, a sol gel process, the ion plating method, an ion-beam-deposition method, an MBE technique, a vacuum deposition method, electron beam evaporation method, etc. besides the above.

[Translation done.]

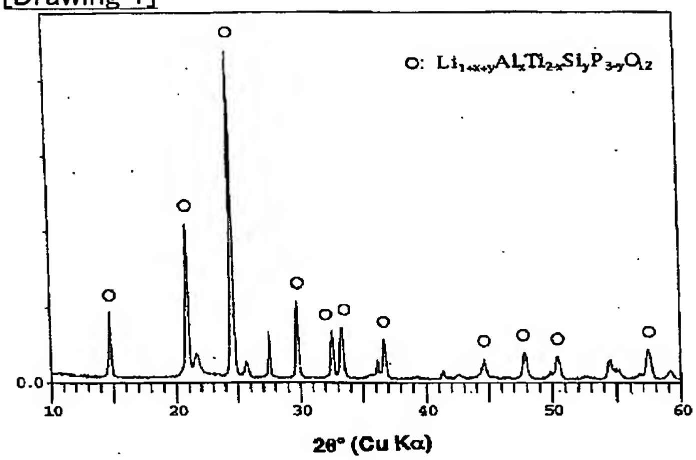
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]Drawing 1 shows the X diffraction pattern of the crystallized glass of Example 1.
[Drawing 2]It is a figure showing a typical structure of the lithium cell which uses the Li-ion solid electrolyte by this invention. This invention is not restricted by this drawing.
[Drawing 3]It is a figure showing a typical structure of the gas sensor which uses the Li-ion solid electrolyte by this invention. This invention is not restricted by this drawing.
[Drawing 4]It is an efficiency discharge characteristic figure of the cell shown in drawing 3.
[Drawing 5]It is an electromotive force characteristic figure by the carbon dioxide partial pressure in the room temperature of the gas sensor shown in drawing 4.
[Description of Notations]
1. Li-ion conductivity crystallized glass
2. Negative electrode
3. Anode
4. Negative-electrode collecting electrode plate
5. Anode current collector
6. Negative electrode can
7. Positive electrode can
8. Insulating packing
9. Metallic carbonate
10. Electrode
11. Li-ion conductivity crystallized glass
12. Electrode
13. Lead
14. Lead
15. Package material

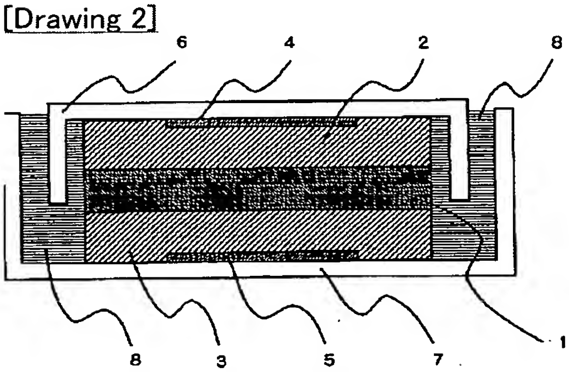
[Translation done.]

DRAWINGS

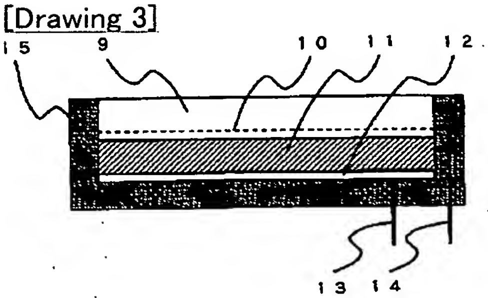
[Drawing 1]



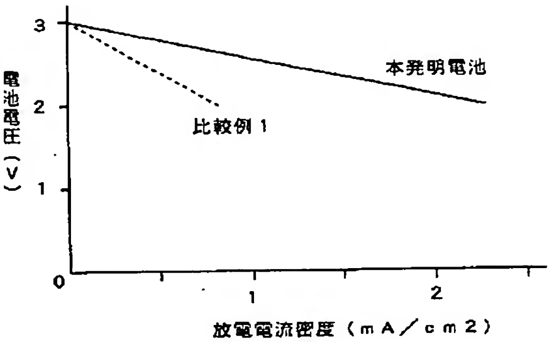
[Drawing 2]



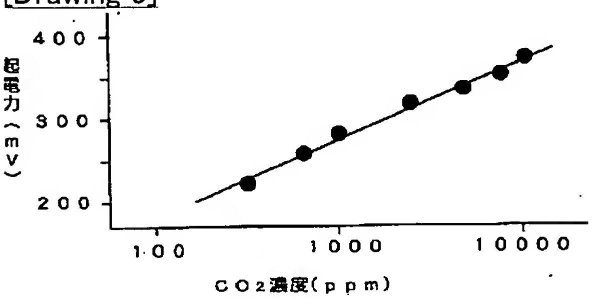
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]

WRITTEN AMENDMENT

-- [Written amendment]
[Filing date]July 30, Heisei 9
[Amendment 1]
[Document to be Amended]Specification
[Item(s) to be Amended]Claim
[Method of Amendment]Change
[Proposed Amendment]
[Claim(s)]
[Claim 1]It is a mol% display,
26 to 40% of P_2O_5
0.5 to 12% of SiO_2
30 to 45% of TiO_2
5 to 10% of M_2O_3 (however, M=aluminum, Ga)
Li_2O 10-18%
Lithium-ion-conductivity crystallized glass which contains and is characterized by depositing $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$ (however, O<=X 0.4, O<Y<=0.6) by heat treatment after melt molding.
[Claim 2]It is a mol% display,
26 to 40% of P_2O_5
0.5 to 12% of SiO_2
32 to 45% of TiO_2
5 to 10% of $aluminum_2O_3$
Li_2O 10-18%
The crystallized glass according to claim 1 which contains and is characterized by depositing $Li_{1+X+Y}aluminum_XTi_{2-X}Si_YP_{3-Y}O_{12}$ (however, O<=X 0.4, O<Y<=0.6) by heat treatment after melt molding.
[Claim 3]It is a mol% display,
26 to 40% of P_2O_5
0.5 to 12% of SiO_2
32 to 45% of TiO_2
5 to 10% of Ga_2O_3
Li_2O 10-18%
The crystallized glass according to claim 1 which contains and is characterized by depositing $Li_{1+X+Y}Ga_XTi_{2-X}Si_YP_{3-Y}O_{12}$ (however, O<=X 0.4, O<Y<=0.6) by heat treatment after melt molding.
[Claim 4]A solid electrolyte for cells using alkaline ion conductivity crystallized glass.
[Claim 5]A solid electrolyte for cells using lithium-ion-conductivity crystallized glass.
[Claim 6]A solid electrolyte for cells using the crystallized glass according to any one of claims 1 to 3.

[Claim 7]A solid state battery characterized by using alkaline ion conductivity crystallized glass as a solid electrolyte.
[Claim 8]A solid state battery characterized by using lithium-ion-conductivity crystallized glass as a solid electrolyte.
[Claim 9]A solid state battery characterized by using the crystallized glass according to claim 1 to 3 as a solid electrolyte.
[Claim 10]A solid electrolyte for gas sensors using alkaline ion conductivity crystallized glass.
[Claim 11]A solid electrolyte for gas sensors using lithium-ion-conductivity crystallized glass.
[Claim 12]A solid electrolyte for gas sensors using the crystallized glass according to any one of claims 1 to 3.
[Claim 13]A gas sensor characterized by using alkaline ion conductivity crystallized glass as a solid electrolyte.
[Claim 14]A gas sensor characterized by using lithium-ion-conductivity crystallized glass as a solid electrolyte.
[Claim 15]A gas sensor characterized by using the crystallized glass according to claim 1 to 3 as a solid electrolyte.
[The amendment 2]
[Document to be Amended]Specification
[Item(s) to be Amended]0001
[Method of Amendment]Change
[Proposed Amendment]
[0001]
[Field of the Invention]Ionic conductivity of this invention is high, and is thermally stable, and manufacture is related with lithium conductivity crystallized glass also in easy ion-conductive crystallized glass.
[Amendment 3]
[Document to be Amended]Specification
[Item(s) to be Amended]0012
[Method of Amendment]Change
[Proposed Amendment]
[0012]
[Problem(s) to be Solved by the Invention]As stated above, the conventional ion-conductive solid electrolyte had low conductivity, and a miniaturization and slimming down had the technical problem were difficult. This invention solves the technical problem of ******, provides crystallized glass with the very high ionic conductivity of reaching $1.5x10^{-3}$S/cm at a room temperature, and is realizing a highly efficient solid state battery and gas sensor using this crystallized glass further.
[Amendment 4]
[Document to be Amended]Specification
[Item(s) to be Amended]0018
[Method of Amendment]Change
[Proposed Amendment]
[0018]The invention according to claim 4 is a solid electrolyte for cells using alkaline ion conductivity crystallized glass for a solid electrolyte. The invention according to claim 5 is a solid electrolyte for cells using lithium-ion-conductivity crystallized glass for a solid electrolyte. The invention according to claim 6 is a solid electrolyte for cells using the crystallized glass according to any one of claims 1 to 3 for a solid electrolyte. The invention according to claim 7 is a solid state battery using the solid electrolyte made from alkaline ion conductivity crystallized glass. The invention according to claim 8 is a solid state battery using the solid electrolyte made from lithium-ion-conductivity crystallized glass. The invention according to claim 9 is a solid electrolyte using the solid electrolyte manufactured using the crystallized glass according to claim 1 to 3.
[Amendment 5]
[Document to be Amended]Specification
[Item(s) to be Amended]0019
[Method of Amendment]Change
[Proposed Amendment]
[0019]The invention according to claim 10 is a solid electrolyte for gas sensors using alkaline ion conductivity crystallized glass for a solid electrolyte. The invention according to claim 11 is a solid electrolyte for gas sensors using lithium-ion-conductivity crystallized glass for a solid electrolyte. The invention according to claim 12 is a

solid electrolyte for gas sensors using the crystallized glass according to any one of claims 1 to 3 for a solid electrolyte. The invention according to claim 13 is a gas sensor using the solid electrolyte made from alkaline ion conductivity crystallized glass. The invention according to claim 14 is a gas sensor using the solid electrolyte made from lithium-ion-conductivity crystallized glass. The invention according to claim 15 is a gas sensor using the crystallized glass according to claim 1 to 3 for a solid electrolyte.

[Amendment 6]
[Document to be Amended]Specification
[Item(s) to be Amended]0024
[Method of Amendment]Change
[Proposed Amendment]
[0024]
[Embodiment of the Invention]The ion-conductive crystallized glass of this invention is producible by the following method. That is, after carrying out weighing of the starting material by a predetermined ratio and mixing uniformly, it puts into a platinum crucible and heat melting is carried out with an electric furnace. First, a raw material is disassembled at 700 **, gas constituents are evaporated, then, temperature is raised to 1400-1500 **, and it fuses at the temperature for 1 to 2 hours. Then, the cast of the melting glass is carried out on a griddle, and tabular glass is produced. In this way, by heat-treating at 680-800 ** about the obtained glass for 24 hours for 12 hours at a temperature succeedingly higher further 200-350 ** than it, The high ion-conductive crystallized glass in which $Li_{1+X+Y}M_XTi_{2-X}Si_YP_{3-Y}O_{12}$ deposits as a main crystal phase is obtained.

[Amendment 7]
[Document to be Amended]Specification
[Item(s) to be Amended]0037
[Method of Amendment]Change
[Proposed Amendment]
[0037]
[Effect of the Invention]As explained above, the ion-conductive crystallized glass by this invention has very high conductivity, and simply [production] and chemically, since [stable] it is thermally strong, it begins a cell (a fuel cell is also included) and a gas sensor, and the application of it to various electrochemical devices is attained.

[Translation done.]